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THE QUANTITATIVE SEPARATION OF MIXTURES OF CERTAIN ACID COAL TAR DYES.

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INTRODUCTION.

The use of immiscible solvents for separating mixtures of acid coal tar colors is discussed in most standard works on the subject. Loomis[1] gives data concerning the solubility of a large number of common dyes, and Seeker[2] has published qualitative separations of Orange I and Naphthol Yellow S from certain other dyes depending on the use of amyl alcohol. In such procedures any variation made in the acidity has been attained by using acids of different degrees of dissociation, as acetic acid and a mineral acid, and not by adding varying amounts of the same acid. Chiefly with the object of making a quantitative separation of the colors permitted in foods (Naphthol Yellow S, Ponceau 3 R, Orange I, Amaranth, Light Green S F Yellowish, Erythrosin and Indigo Carmin),[3] their ratios of distribution between dilute hydrochloric acid of different concentrations and certain immiscible solvents were determined.[4] The data indicated a method that gives good results in practice and is of quite general applicability. Some figures have also been obtained for other similar colors that will show where separations can be made and can also be applied for qualitative differentiations.

DATA OBTAINED.

In the accompanying table the figures given show the percentage of color remaining in the aqueous layer after shaking with an equal volume of the immiscible solvent. A solution containing a quantity of dye equivalent to 0.1000 gram of pure color was diluted to 50 cc with water and standardized hydrochloric acid, sufficient of the latter being taken to give the solution exactly the acid normality desired. It was then shaken out with 50 cc of the solvent. (This shaking

[1] U. S. Dept. Agr., Bureau of Chemistry Cir. 63.

[2] Allen's Commercial Organic Analysis, 4th ed., vol. 5.

[3] U. S. Dept. Agr., Office of the Secretary, Food Inspection Decision 76.

[4] Distribution ratios of the permitted dyes between dilute hydrochloric acid and amyl alcohol were sent out by the writer in April, 1911, in a circular letter in connection with the cooperative work of the Association of Official Agricultural Chemists.

was continued for five minutes with dichlorhydrin, two minutes with the other solvents.) After separation of the liquids, which takes place very rapidly with strongly acid mixtures but more slowly with low acid concentrations, the lower layer was drawn off and the percentage of dye remaining in the water layer estimated. All color determinations were made by Knecht and Hibbert's method,[1] a standard solution of pure amaranth being used to titrate back any excess of titanium chlorid added. The extractions were made at room temperature, 27° to 30° C.

Of the coloring matters used, the permitted food colors were from analyzed commercial samples of excellent grade. The others were commercial samples of good quality, their examination, however, being limited in most cases to a determination of total color and a comparison of their reactions with the description given in Heumann and in Schultz and Julius (translated and enlarged by A. G. Green, 1904). The serial numbers used in the latter work are given with the names of the dyes.

TABLE 1.—*Percentage of color in the water solution after shaking with an equal volume of immiscible solvent.*

SOLVENT: AMYL ALCOHOL.

Colors.	Normality of hydrochloric acid in water layer before shaking—							
	4	2	1	½	¼	⅛	1/16	1/32
	Percentage of color in water solution after shaking.							
Naphthol Yellow S No. 4	.....	.....	4	7	11	17	27	43
Orange I No. 85	.....	.....	.....	.....	0.5	1	2	4
Ponceau 3 R No. 56	.....	1	3	7	21	43	64	78
Amaranth No. 107	5	15	52	82	93	.....	.....	.....
Light Green S F No. 435	90	95	97	99	99	.....	.....	.....
Erythrosin No. 517	.....	.....	.....	.....	.....	.....	.....	0.0
Indigo Carmin No. 692	34	51	89	96	99	.....	.....	.....
Fast Yellow No. 8	36	.....	61	.....	.....	.....	.....	.....
Crocein Orange G No. 13	.....	.....	.....	.....	.....	.....	1	2
Orange G No. 14	.....	.....	18	.....	58	.....	.....	.....
Ponceau 2 R No. 55	.....	2	.....	14	.....	.....	.....	.....
Crystal Ponceau No. 64	.....	.....	.....	.....	8	.....	30	.....
Fast Red B No. 65	.....	.....	2	.....	16	.....	62	.....
Resorcin Yellow No. 84	.....	.....	.....	.....	5	.....	11	17
Orange II No. 86	.....	.....	.....	.....	.....	.....	2	3
Brilliant Yellow S No. 89	.....	.....	73	.....	90	.....	.....	.....
Tartrazin No. 94	.....	.....	47	.....	88	.....	.....	.....
Metanil Yellow No. 95	.....	.....	.....	.....	.....	.....	1	1
Fast Red A No. 102	.....	.....	.....	.....	.....	.....	0 2	1
Fast Red C No. 103	.....	.....	1	.....	4	.....	.....	.....
Fast Red E No. 105	.....	.....	1	.....	17	.....	68	.....
New Coccin No. 106	.....	15	.....	.....	75	.....	.....	.....
Scarlet 6 R No. 108	41	80	95	.....	.....	.....	.....	.....
Resorcin Brown No. 137	.....	.....	.....	.....	8	.....	20	.....
Cotton Scarlet 3 B No. 136	.....	.....	.....	.....	2	.....	10	.....
Congo Red No. 240 [2]	.....	.....	.....	.....	.....	.....	.....	.....
Azo Blue No. 287 [3]	.....	.....	.....	.....	.....	.....	.....	.....
Chrysophenin No. 329	.....	.....	.....	.....	.....	.....	1	2
Guinea Green B No. 433	.....	.....	48	.....	32	.....	25	.....
Acid Magenta No. 462	75	.....	93	.....	.....	.....	.....	.....

[1] New Reduction Methods in Volumetric Analysis. 1910.
[2] Color acid nearly insoluble in both layers.
[3] Similar to Congo Red but color acid more soluble in alcohol.

SOLVENT: DICHLORHYDRIN.

Naphthol Yellow S No. 4			15					
Ponceau 3 R No. 56			37					
Orange I No. 85			4					
Amaranth No. 107			95					
Light Green S F No. 435			15		17			
Indigo Carmin No. 692			91					
Acid Magenta No. 462			86					

SOLVENT: AMYL ACETATE.

Naphthol Yellow S No. 4	22	33	48					
Ponceau 3 R No. 56	95	96	97					

SOLVENT: ETHER.

Naphthol Yellow S No. 4		94	97					
Orange I No. 86		97	97					

DISCUSSION OF RESULTS.

In applying the data given in the table for effecting the quantitative separation of two colors the following procedure, or some simple modification of it, has been practiced. The solution containing 0.2 to 0.4 gram of color (depending on the nature of the dyes) is treated with sufficient water and hydrochloric acid of known strength to bring its volume to about 50 cc and its acid concentration to that point for which the difference in percentage of color extracted for the two dyes is near its maximum. The solution is then shaken out with the immiscible solvent, being passed in succession through three or four separatory funnels each containing 50 cc of the latter. The portions of the solvent are washed with 50 cc of hydrochloric acid of the same normality as the solution, being passed successively through the separatory funnels in the same order as was the original solution, and this operation is repeated with one or two fresh amounts of the hydrochloric acid. The dye relatively more soluble in water is determined in the combined washings and extracted solution. The second dye is removed from the solvent by shaking with water, very dilute caustic soda, or, more quickly, with dilute caustic soda after the addition of some gasoline, or similar substance in which the color is insoluble.

Assuming the distribution ratios to remain constant, this procedure using four funnels and making three washings gives for a pair of colors whose "distribution numbers" (as the percentage numbers given in the table may be called) are 80 and 20, respectively, a separation of 98.30 per cent for each color. With distribution numbers 90 and 10 four funnels and three washings give a calculated separation of 99.73 per cent, and the same is obtained with distribution numbers 81.8 and 5.3 if the solvent in which the dyes are relatively more soluble be taken in portions one-half the volume of those of the other liquid. If the second, third, and fourth funnels be given

a fifth washing, the third and fourth funnels a sixth, and the last funnel a seventh washing, the calculated loss for the color more soluble in the solvent layer is 0.76 per cent, while the percentage of the other dye removed is relatively much increased (to 99.99 per cent). In most mixtures the progress of the separation is always apparent.

In practice, because of incomplete extraction and separation, and especially on account of uncertainty due to small amounts of subsidiary dyes always present, it is necessary to increase the number of successive extractions. The formation of esters of the color acids is a possible source of difficulty, but is not believed to take place. With amyl alcohol as solvent it is almost always desirable to make the original solution more strongly acid than is indicated by the distribution data and use relatively more portions of the washing liquid.

Of the permitted colors, Naphthol Yellow S is best separated from Orange I by washing the amyl alcohol solution of the color acids with strong salt solution, care being taken that not too much color is present. With a solution containing 20 grams of salt and 0.04 gram Naphthol Yellow S per 100 cc and shaken with an equal volume amyl alcohol, 97 per cent of the color is retained by the water. With a similar solution containing 0.07 gram Orange I, the water layer contains 1.5 per cent of the total color. With higher concentrations some color may be salted out in solid form, but this does not interfere if the amount is small. Erythrosin being quantitatively removed from slightly acid solutions by amyl acetate, ether, or amyl alcohol, its separation from sulphonated colors presents no difficulty.

ANALYSES OF MIXTURES.

Analyses of a number of mixtures were made with the following results. In all cases the last washings were free or practically free from colors. As the determination of total color is convenient and accurate, it was in most cases made together with that of the dye reacting with the lesser amount of titanium trichlorid.

Naphthol Yellow S and Light Green S F Yellowish.

Twenty cc of a solution containing in this volume 0.1000 gram green and 0.1083 gram yellow was treated with 20 cc five-normal hydrochloric acid and diluted to 50 cc, then shaken out with three portions of amyl alcohol of 50 cc each. The amyl alcohol was washed with two portions (50 cc each) of two-normal hydrochloric acid. Green was determined in the extracted solution and washings, total color in another aliquot of the original solution.

Green, found 0.0975 gram = 97.5 per cent.

Yellow, found 0.1085 gram = 100 per cent.

Naphthol Yellow S, Orange I, and Indigo Carmin.

Thirty cc of solution containing 0.1000 gram Orange, 0.1000 gram Blue, and 0.1083 gram Yellow was treated with 2 cc five-normal hydrochloric acid and shaken through three funnels containing each 60 cc amyl alcohol. The latter was then washed with two portions of dilute hydrochloric acid (2 cc five-normal hydrochloric acid + 28 cc water, or one-third normal). The second and third funnels were then washed with a third portion of acid (30 cc) and the third funnel with a fourth portion. The Blue was determined directly in the extracted solution and washings.

The amyl alcohol was then washed with four portions of 120 cc each sodium chlorid solution (200 grams per liter). The second and third funnels were washed a fifth time and the third a sixth time.

Blue, found 0.099 gram = 99 per cent.

Orange, found 0.0985 gram = 98.5 per cent.

Total color was determined and Yellow estimated by difference.

Yellow, found 0.1080 gram = 99.5 per cent.

Ponceau 3 R and Naphthol Yellow S.

Twenty cc of solution containing 0.1083 gram Yellow and 0.1168 gram Ponceau was treated with 20 cc concentrated hydrochloric acid and passed through four funnels containing each 60 cc of amyl acetate. The amyl acetate portions were washed with 3 portions of 30 cc each of four-normal hydrochloric acid, a fourth washing given to the last three funnels, a fifth to the last two, and a sixth to the last one. The amyl acetate solution was diluted with gasoline, the Ponceau removed by washing with very dilute caustic soda and determined in this solution. Total color was determined and Yellow estimated by difference.

Ponceau, found 0.1132 gram = 97 per cent.

Yellow, found 0.1089 gram = 100.5 per cent.

Amaranth and Orange I.

Twenty cc of solution containing in this volume 0.1000 gram Orange and 0.1723 gram Amaranth was treated with 2 cc five-normal hydrochloric acid and 28 cc water and passed through two funnels containing 50 cc each of amyl alcohol. The latter were then washed twice with 50 cc volumes of eighth-normal hydrochloric acid. Amaranth was determined directly in the extracted solution and washings. Total color was determined in an aliquot of the original solution.

Amaranth, found 0.1731 gram = 100.5 per cent.

Orange, found 0.0995 gram = 99.5 per cent.

Light Green S F Yellowish, Amaranth, Ponceau 3 R, and Orange I.

Thirty-seven cc solution containing in this volume 0.1000 gram Green, 0.1000 gram Ponceau, 0.1000 gram Orange, and 0.1162 gram Amaranth was treated with 20 cc of concentrated hydrochloric acid and shaken through three funnels containing each 50 cc amyl alcohol. The latter was washed with three portions (50 cc) of four-normal hydrochloric acid. Green was determined in the extracted solution and washings.

Two more funnels containing 50 cc portions of amyl alcohol were now added and the series washed with five 50 cc amounts of fourth-normal hydrochloric acid. The first washing was colorless on coming from the fourth funnel and was discarded. The second, third, fourth, and fifth funnels were given a sixth additional washing, the last three a seventh, the last two an eighth, and the last one a ninth. The extracted solution and washings were combined, nearly neutralized with two-normal ammonium hydroxid, evaporated to about 150 cc, and Amaranth determined.

A second portion of 37 cc of the original solution was treated with 2 cc of five-normal hydrochloric acid and made up to 75 cc, then shaken out with four 25 cc portions of amyl alcohol. These were washed with five portions (75 cc each) sixteenth-normal hydrochloric acid. The last three funnels were given a sixth washing, the last two a seventh, and the last one an eighth. The amyl alcohol was then diluted with gasoline, the Orange removed with dilute caustic soda and estimated. Total color was determined in an aliquot of the original solution and the Ponceau found by difference.

Green, found 0.098 gram = 98 per cent.
Amaranth, found 0.116 gram = 100 per cent.
Orange, found 0.102 gram = 102 per cent.
Ponceau, found 0.098 gram = 98 per cent.

Ponceau 3 R and Indigo Carmin.

Twenty-eight cc of solution containing 0.1000 gram Ponceau and 0.1000 gram Blue was treated with 2 cc five-normal hydrochloric acid and shaken with four 50 cc portions of amyl alcohol. Three portions (50 cc each) of third-normal hydrochloric acid were then passed through the series of funnels, a fourth washing given to the last three, a fifth to the last two, and a sixth to the last one. Blue was determined directly in the extracted solution and washings. Total color was estimated and the Ponceau obtained by difference.

Blue, found 0.102 gram = 102 per cent.
Ponceau, found 0.099 gram = 99 per cent.

Light Green S F Yellowish and Indigo Carmin.

Twenty-three cc solution containing 0.1000 gram Blue and 0.1000 gram Green was treated with 2 cc five-normal hydrochloric acid and shaken out with six 25 cc portions of dichlorhydrin (saturated with water). The dichlorhydrin portions were passed successively through four funnels containing each 25 cc of fourth-normal hydrochloric acid saturated with dichlorhydrin. They were then combined, diluted with benzol, the color removed with water, and titrated. Total color was determined and Blue found by difference.

Green, found 0.099 gram = 99 per cent.
Blue, found 0.101 gram = 101 per cent.

Naphthol Yellow S and Amaranth.

A 10 cc solution containing 0.1273 gram Amaranth and 0.1083 gram Yellow was treated with an equal volume of concentrated hydrochloric acid and shaken through three funnels containing each 40 cc amyl acetate. The amyl acetate portions were then washed with 20 cc of six-normal hydrochloric acid and the last two funnels given a second washing. The Amaranth was determined in the extracted solution and washings. The Naphthol Yellow S was removed from the amyl acetate by washing with a little dilute caustic soda solution and determined directly.[1]

Amaranth, found 0.128 gram = 101 per cent.
Yellow, found 0.108 gram = 100 per cent.

In using the table to distinguish qualitatively between such colors as Amaranth and the other Fast Reds, or Guinea Green and Light Green S F Yellowish, it must be remembered that the relative intensity of the coloration of the two layers is usually somewhat different from their relative concentration and may be very much so.

[1] Naphthol Yellow S is conveniently titrated in tartrate solution, a little Light Green S F Yellowish being added to serve as indicator.

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